Supporting information

For

A magnetic molecularly imprinted optical chemical sensor for specific recognition of trace quantities of virus

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Optimization of the assay conditions

The following experiments were designed referee to our previous work. The thickness of MIPs layer can be adjusted with DA concentrations. So the HAV-imprinted Fe_3O_4@PDA NPs were prepared by adjusting with DA amount. And then 1 nmol·L^{-1} of HAV were adsorbed by the resultant MIPs (**Table.S1**). From the results we can see, when the mass ratio of Fe_3O_4: HAV: DA was 150 mg: 13.7 mg: 50 mg, the adsorption effect were best than others, it can be explained that smaller amount of dopamine leading to the thinner PDA film, hence the structures of imprinting sites were easy destroyed during eluting. With the increasing of the amount of DA, the ΔI_{RLS} achieved highest when the mass ratio of Fe_3O_4: HAV: DA was 150 mg: 13.7 mg: 50 mg, and then slightly decreased, the reason is too thick is not conducive to the elution of the template and difficult to leave sites to bond new template molecules. Hence, this mass ratio was selected for our synthesis.

To obtain a sensitive and practical assay for HAV detection, we studied various factors that could potentially affect the light scattering efficiency, such as the virus magnetic-MIPs dosage **(Fig. S2)**, pH (**Fig. S3**), and incubation time (**Fig. S4**). These factors were optimized by the "one-at-a-time" method.

The virus magnetic-MIPs dosage (30–120 ng·mL^{-1}) was investigated for a constant initial concentration of HAV to achieve the maximum number of possible RLS signal variations. The results showed that the RLS intensity obviously increased with rising concentration of virus magnetic-MIPs when the intensity was lower than 90 ng·mL^{-1}. At this stage, a surplus of HAV was available. The increase in the virus magnetic-MIPs concentration indicated more recognition sites, which led to the capture of more HAV and the formation of large volumes of complexes. [1] Thus, the RLS intensity continued to increase until the adsorption amount of virus magnetic-MIPs reached the saturation value, all of HAV in the solution were adsorbed just. Meanwhile, the higher concentration led to less adsorbent saturation in the system and caused the decreased amount of HAV adsorbed on each HAV-imprinted polymer NP. Thus, the RLS intensity decreased. The dosage of 90 ng·mL^{-1} produced the maximum signal variation, so this dose was selected for further optimization.

The RLS intensity increased as the pH increased in the range of 5.0–6.7 (**Fig. S3**). According to the principle of RLS, this trend was due to the interaction between virus magnetic-MIPs and HAV, which led to large volumes of formed complexes. [1-3] When the pH was higher than 6.7, the RLS intensity decreased with increasing pH. This trend could be explained as follows. The isoelectric point of HAV is 7.15; HAV is positively charged when the pH is lower than the isoelectric point (7.15). Meanwhile, the pH_{PZC} of the PDA materials is approximately 4.0, and the PDA materials are negatively charged when the pH is higher than 4.0. [4, 5] within the pH range of 4.0–7.15, the negative charge of PDA increased with increasing pH, whereas the positive value of HAV was weakened. Inevitably, the optimal pH was obtained, which produced the maximum static electricity between PDA and HAV. The experimental results revealed that the optimal pH value was 6.7. Therefore, pH 6.7 was selected as the optimal pH for further research.

The reaction time of HAV with the virus magnetic-MIPs is presented in **Fig. S4.** A rapid increase in the RLS intensity was observed, and the reaction process almost reached equilibrium after 150 min, which was consistent with the literature. [6]

Reference

[1] R.F. Pasternack, C. Bustamante, P.J. Collings, A. Giannetto, E.J. Gibbs, J. Am. Chem. Soc. 1993, **115**, 5393-5399.
[2] W. Hergert, T. Wriedt, The Mie theory. Basics and applications, Springer, Berlin. 2012.
[3] H.H. Cai, P.H.Yang, J. Chen, Z.H. Liang, Q.Chen, J. Cai, *Electrochim. Acta,* 2009, **54**, 3651-3656.
[4] B. P. Lee, P. B. Messersmith, J. N. Israelachvili, J. H. Waite, Annu. Rev. Mater. Res. 2011, **41**, 99-132.
[5] C.C.Ho, S. J. Ding, J. Mater. Sci.Mater. Med. 2013, **24**, 2381-2390.
[6] Z. Xia, Z. Lin, Y. Xiao, L. Wang, J. Zheng, H. Yang, G. Chen, Biosens. Bioelectron. 2013, **47**, 120-126.

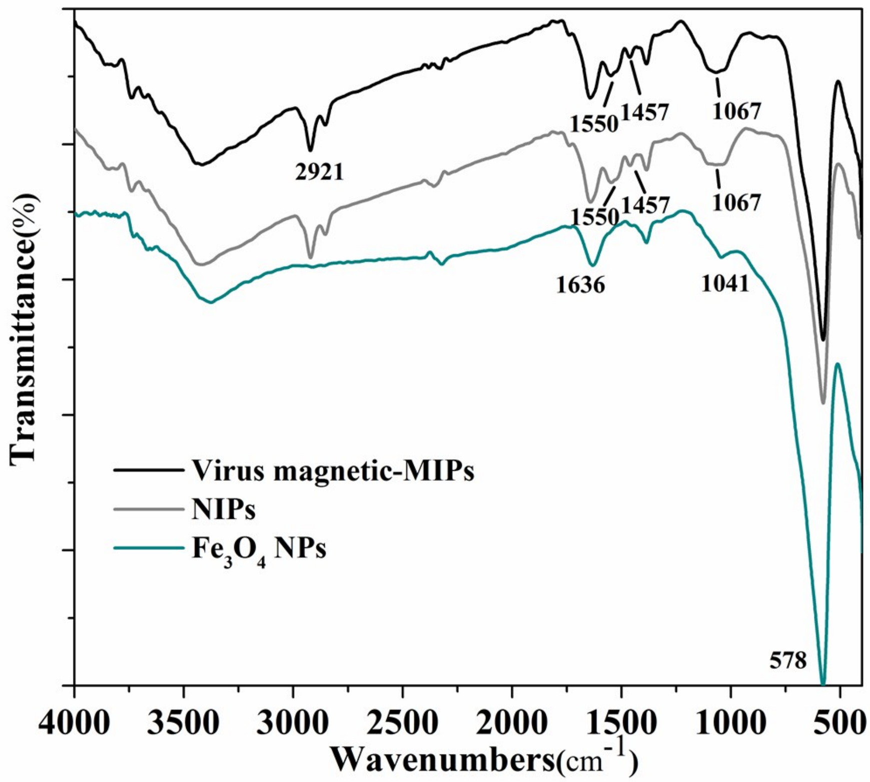

Fig. S1 FT-IR spectra of Fe_3O_4 NPs, NIPs, virus magnetic-MIPs

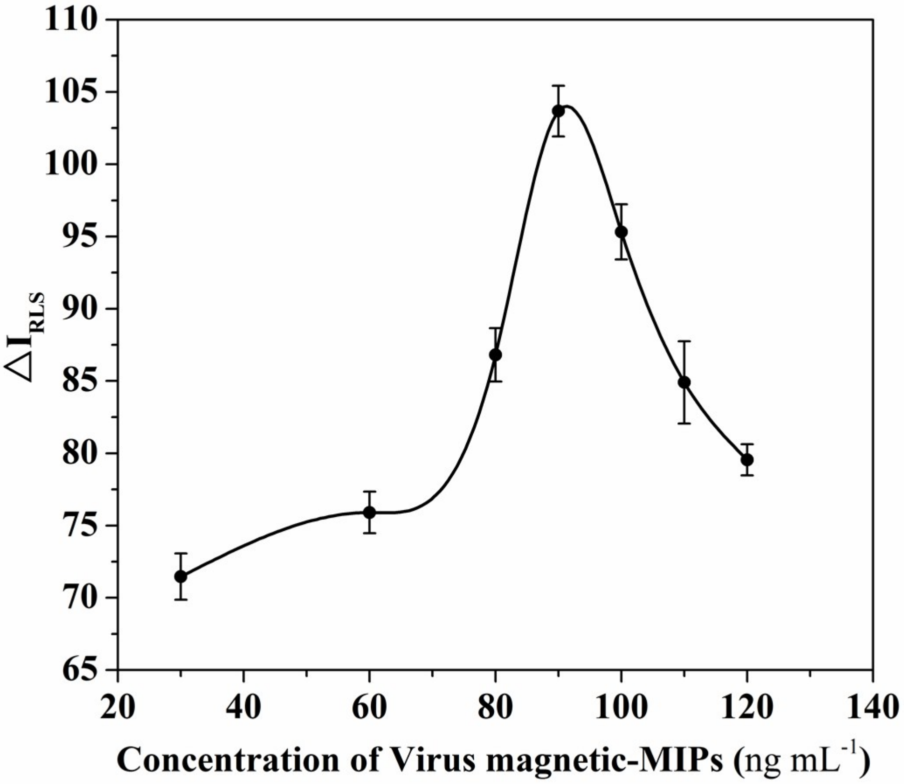

Fig. S2 Effect of virus magnetic-MIPs dosage on the RLS signal

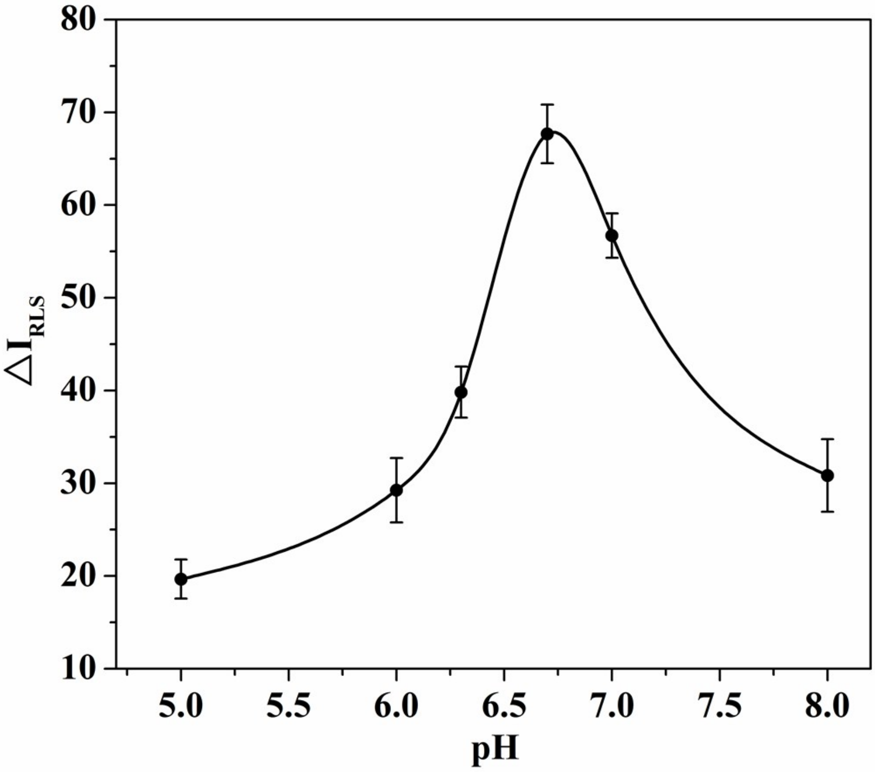

Fig. S3 Effect of pH on the RLS signals of the virus magnetic-MIPs

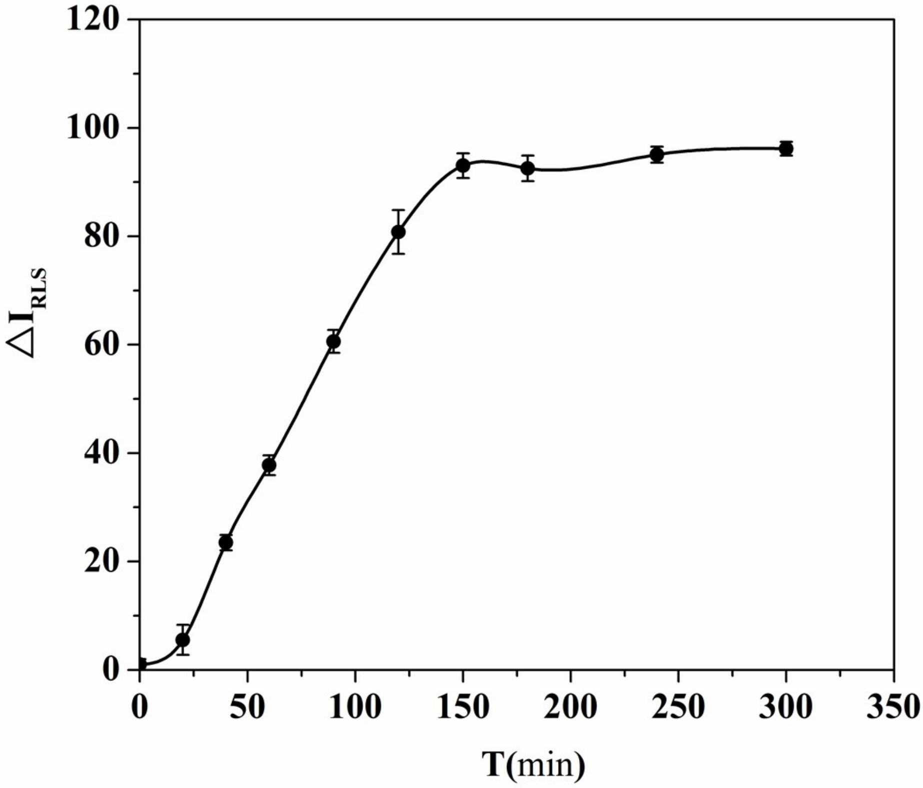

Fig. S4 Effect of reaction time on the RLS signals of the virus magnetic-MIPs

Table.S1 The influence of DA amount on HAV imprinting and recognition

	Fe_3O_4: HAV: DA				
	150:13.7:30	150:13.7:40	150:13.7:50	150:13.7:60	150:13.7:70
ΔI_{RLS}	173.5	214	250	220	198